

PATENT SPECIFICATION

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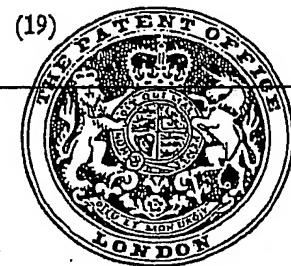
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(54) POLYESTER COMPOSITIONS

(71) We, TEIJIN LIMITED, a Japanese body corporate, of No. 1 Umeda, Kita-Ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to compositions comprising an aromatic polyester resin and a polycarbonate resin with inhibited coloration, and to a method for inhibiting the coloration of such compositions.

We have investigated the possibility of improving the heat-distortion temperature of aromatic polyester resins, derived from a glycol component at least 70 mol % of which consists of tetramethylene glycol and an acid component at least 70 mol % of which consists of isophthalic acid, terephthalic acid, a naphthalene dicarboxylic acid, or a polyester-forming derivative thereof which are polymerized with a titanium compound catalyst, by blending them with a polycarbonate resin, without impairing their high rate of crystallization, excellent moldability under normal molding conditions, and superior chemical resistance and abrasion resistance, which properties make them suitable as materials for injection molding or extrusion molding. During our investigations, we have found that a blend comprising such a aromatic polyester resin composed mainly of tetramethylene aryl dicarboxylate units and a polycarbonate resin assumes a yellow color. This coloring phenomenon is not an ordinary coloring phenomenon occurring as a result of degradation of the polyester resin, but occurs as a result of the mixing of the two resins. We have now discovered that this unique coloring phenomenon can be inhibited by incorporating into the blend of the polyester and the polycarbonate a phosphorus compound in a much smaller amount than required for producing a fire-retarding effect. The phosphorus compounds (3) (see below) are known as stabilizers for inhibiting the degradation of polyester resins such as poly(ethylene terephthalate) due to

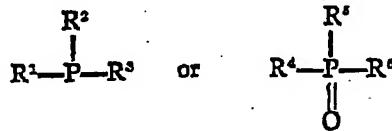
the reaction catalyst such as calcium acetate or manganese acetate, and also include those phosphorus compounds which are generally known as fire-retarding agents.

Accordingly, the present invention provides an aromatic polyester resin composition with inhibited coloration which comprises:

1. 100 parts by weight of an aromatic polyester resin derived from a glycol component at least 70 mol % of which consists of tetramethylene glycol and an acid component at least 70 mol % of which consists of isophthalic acid, terephthalic acid, and naphthalene dicarboxylic acid, or a polyester forming derivative thereof, which components are polymerized with a titanium compound catalyst,

2. 5 to 100 parts by weight of a polycarbonate resin, per 100 parts by weight of the aromatic polyester resin, and

3. 0.01 to 3 parts by weight per 100 parts by weight of the aromatic polyester resin of at least one phosphorus compound which is liquid or solid at room temperature and is of formula:



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wherein each of R¹ to R⁶ independently represents hydrogen, alkyl of 1 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, aralkyl of 7 to 20 carbon atoms, or —OR in which R is hydrogen, alkyl, hydroxyalkyl or cycloalkyl of up to 20 carbon atoms, aryl of 6 to 20 carbon atoms, or aralkyl of 7 to 20 carbon atoms; or R¹, R² and R³, or R⁴, R⁵ and R⁶ together with the phosphorus atom to which they are attached form a ring, and/or a metal salt thereof.

The aromatic polyester resin (I) can be obtained by polymerizing a glycol component at least 70 mol %, preferably at least 80 mol %, of which consists of tetramethylene

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5 glycol and an acid component at least 70 mol %, preferably at least 80 mol %, of which consists of isophthalic acid, terephthalic acid, a naphthalenedicarboxylic acid, or a polyester-forming derivative thereof, in the presence of a titanium compound as a catalyst. The amount of polycarbonate employed is 5 to 100 parts by weight, preferably 10 to 70 parts by weight, per 100 parts by weight of the aromatic polyester resin. If the proportion of the polycarbonate is less than 5 parts by weight, the heat distortion temperature of the aromatic polyester increases only slightly to a degree which is not practicable. If the proportion exceeds 100 parts by weight, the excellent properties of the polyester, such as moldability or chemical resistance, are impaired. 70

10 The glycol component can contain not more than 30 mol %, preferably not more than 20 mol %, of another glycol, such as ethylene glycol, trimethylene glycol, hexamethylene glycol, decamethylene glycol, cyclohexane dimethyol, or neopentylene glycol. 75

15 The acid component can be a derivative of the specified acids, for example a C_1-C_8 alkyl ester. Examples of naphthalenedicarboxylic acids are 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid and 1,5-naphthalenedicarboxylic acid, and polyester-forming derivatives thereof can of course be used. 80

20 The acid component can contain not more than 30 mol %, preferably not more than 20 mol %, of another acid, such as 4,4'-diphenyldicarboxylic acid, 4,4'-diphenoxycyclohexane-dicarboxylic acid, p-hydroxybenzoic acid, sebacio acid, or adipic acid. 85

25 The aromatic polyester resin (1) preferably has an intrinsic viscosity $[\eta]$ (measured in o-chlorophenol at 35°C) of 0.3 to 1.5. 90

30 The polycarbonate resin (2) is preferably aromatic and is preferably a polycarbonate of a di(monohydroxyphenyl)-substituted aliphatic hydrocarbon, for example an aromatic polycarbonate derived by the ester interchange process or phosgene process from 2,2-bis(4-hydroxydiphenyl)-propane (namely bis-phenol A), or 1,1'-bis(4-hydroxyphenyl)-cyclohexane (namely bisphenol Z). A part or whole of the bisphenol A may be replaced by another 4,4'-di-hydroxydiphenyl alkane, 4,4'-dihydroxydiphenyl sulfone, or 4,4'-dihydroxydiphenyl ether. Alternatively, two or more of such aromatic polycarbonates may be used. 100

35 Preferred polycarbonate resins have a number average molecular weight of 10,000 to 100,000. 105

40 It is essential to employ aromatic polyesters obtained by polymerization in the presence of a titanium compound as catalyst in the compositions of the present invention because the unique coloring phenomenon is not due to the degradation of polyester and occurs only in a blend of the polycarbonate resin with the aromatic polyester resin obtained by using the above catalyst. Examples of titanium compounds which can be employed as catalyst are titanium tetrabutoxide, titanium tetrakisopropoxide, titanium tetrachloride, titanium oxalate, titanium potassium oxalate, amorphous titanium dioxide or potassium titanate fluoride. The amount of the titanium catalyst generally is 0.001 to 1 mol %, preferably 0.005 to 0.5 mol %, based on the weight of the polyester. 110

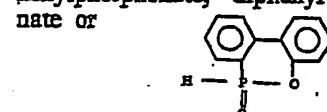
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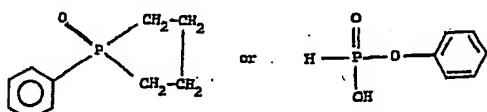
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5 phosphinic acid; mono- or disubstituted phosphinic acid such as phenylphosphinic acid, dimethylphosphinic acid, diphenylphosphinic acid; phosphinic acid esters such as methyl dimethylphosphinate, phenyl methylphosphinate, phenyl diphenylphosphinate, phenyl diphenylphosphonite, methyl diphenylphosphonite, or triphenyl phosphine, triphenyl phosphine oxide or a phosphorus compound of the formula:



10 It is also possible to use metal salts of phosphorus compounds, for example salts of compounds selected from phosphoric acid, phosphorous acid, phosphonic acid, phosphonous acid, phosphinic acid, phosphinous acid, substituted phosphonic acid, such as methylphosphonic acid and phenyl phosphonic acid, di- or mono-substituted phosphinous acid such as diphenyl phosphinous acid, and metals selected from lithium, sodium, potassium, rubidium, caesium, magnesium, calcium, strontium, barium, manganese, iron, cobalt, nickel, zinc, silver, cadmium, aluminium, tin, and lead. 15 The alkali metal salts and alkaline earth metal salts are especially preferred. Specific examples of metal salts are monosodium phosphate, disodium phosphate, trisodium phosphate, calcium phosphate, aluminium phosphate, monopotassium phosphite, calcium phosphite, magnesium phosphite, di-sodium phenylphosphonate, magnesium phenylphosphonate, mono-sodium methylphosphonite, potassium phosphonate, and sodium diphenylphosphonite.

20 The amount of the phosphorus compound or its metal salt employed is 0.01 to 3 parts by weight, preferably 0.01 to 1 part by weight, especially 0.02 to 0.5 part by weight, per 100 parts by weight of the aromatic polyester resin. This amount is smaller than that required to impart fire retardancy to the polyester but is sufficient to inhibit coloration.

25 The compositions of this invention can be prepared by mixing the polyester, the polycarbonate and the phosphorus compound at any desired stage before the completion of melt-shaping. For example, the following methods can be used.

30 (1) The phosphorus compound or its metal salt is added to a raw material for preparing the polyester or to an intermediate product formed during the polymerization, and the resulting polyester is melt-mixed with the polycarbonate during molding or before.

35 (2) The phosphorus compound or its metal salt is adhered to or mixed with the polyester after polymerization, and the blend is melt-mixed with the polycarbonate during or before molding.

(3) The phosphorus compound is mixed with or adhered to the polycarbonate, and the resulting mixture is melt-mixed with the polyester during or before molding.

(4) The polyester, the polycarbonate, and the phosphorus compound are simultaneously mixed during or before molding.

(5) A solution of the polyester, the polycarbonate and the phosphorus compound in a solvent is prepared, and after uniform mixing, the solvent is removed.

In order to inhibit any change in properties as a result of an inter-reaction of the polyester with the polycarbonate during melt-mixing, it is preferred to limit the period of melt-mixing to not more than 30 minutes, especially to not more than 10 minutes.

The compositions of this invention can further contain various additives such as anti-oxidants, light stabilizers, pigments, fire-retardants, crystallization promoters, reinforcing agents (for example, glass fibers), fillers and/or mold releasing agents.

The compositions of this invention have a high heat distortion temperature, and superior abrasion resistance, chemical resistance, and color.

The following Examples illustrate the present invention. In the Examples, all parts are by weight. The intrinsic viscosity, the heat distortion temperature, and the color were measured by the following methods.

Intrinsic viscosity [η]

Measured on an o-chlorophenyl solution at 35°C.

Heat-distortion temperature

Measured in accordance with ASTM D-648 using a test piece (5" x $\frac{1}{4}$ " x $\frac{1}{2}$ ") under a load of 264 p.s.i.

Color

Cylindrical pellets (average diameter of about 1.5 mm and average length of about 5 mm) were maintained in air at 140°C. for 1 hour, and then L, a and b values of the pellets were measured using a Hunter-type color meter. The values indicated are average values of 10 pellets.

100 Examples 1 to 17 and Comparative Examples 1 to 3.

Preparation of poly(tetramethylene terephthalate):—

110 A reactor equipped with a stirrer was charged with 194 parts of dimethyl terephthalate, 135 parts of tetramethylene glycol and 0.068 part of titanium tetrabutoxide, and heated to 150 to 220°C. Methanol which formed as a result of the reaction was distilled out of the reactor throughout the reaction. Substantially the theoretical amount of methanol was distilled off. The reaction temperature was gradually raised to 250°C. The

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reaction mixture was maintained at this temperature, and the pressure of the inside of the reactor was gradually reduced to about 0.5 mmHg over the course of 1 hour. The reaction was carried out at this pressure for an additional one hour. The resulting poly(tetramethylene terephthalate) had an intrinsic viscosity of 0.72.

5 Preparation of composition:—

10 The resulting polytetramethylene terephthalate was dried for 5 hours at 120°C., and then mixed with a polycarbonate of 2,2-bis(4-hydroxyethyl phenyl) propane having an intrinsic viscosity of 0.68, and each of the phosphorus compounds indicated in Table 1 in the amounts indicated in Table 1. The mix-

ture obtained was melt-mixed and extruded at 250°C. using an extruder to form pellets (cylindrical pellets each having a diameter of about 1.5 mm and a length of about 5 mm). The color and intrinsic viscosity of the pellets, and the heat distortion temperature and elongation of test pieces obtained by melt-shaping the pellets are shown in Table 1.

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For comparison, the above procedure was repeated except that the phosphorus compound was not added (Comparative Example 1), a larger amount of the phosphorus compound was added (Comparative Example 2), and an antioxidant was added instead of the phosphorus compound (Comparative Example 3). The results are also shown in Table 1.

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TABLE 1

	Composition					Properties of Composition					
	Polytetra-methylene-terephthalate (parts)	Poly carbonate (parts)	Phosphorous compound	Type	Amount (parts)	Color	L	a	b	Intrinsic viscosity $[\eta]$	Heat distortion temperature (°C)
Example 1	90	10	triphenyl phosphite		0.5	71.8	-1.0	3.8	0.71	70	310
Example 2	80	20	Phosphorous acid		0.05	72.9	-0.9	3.2	0.71	86	280
Example 3	70	30	trimethyl phosphite		0.3	70.4	-0.5	3.9	0.70	105	210
Example 4	70	30	phosphoric acid		0.02	72.1	-0.2	4.1	0.69	104	220
Example 5	70	30	trimethyl phosphate		0.2	74.2	-0.1	3.7	0.70	105	215
Example 6	70	30	phenyl phosphonic acid		0.05	75.2	-1.1	5.1	0.70	105	230
Example 7	60	40	triphenyl phosphine		0.5	76.8	-1.2	5.3	0.69	110	200
Example 8	90	10	monosodium phosphate		0.05	73.2	-0.9	3.2	0.70	71	300
Example 9	80	20	aluminium phosphite		0.10	73.2	-0.8	3.1	0.71	86	290
Example 10	70	30	disodium phosphate		0.05	76.5	-1.1	3.7	0.70	104	280

TABLE 1 (continued)

	Composition						Properties of Composition				
	Polytetra-methylene-terephthalate (parts)	Poly carbonate (parts)	Phosphorus compound		Amount (parts)	Color	Intrinsic viscosity [η]	Heat distortion temperature (°C)	Elongation (%)		
			Type	Amount (parts)					L	a	
Example 11	70	30	monosodium phosphite	0.3	76.8	-0.3	3.5	0.71	105	225	225
Example 12	70	30	disodium phosphite	0.5	73.1	-0.3	3.8	0.69	105	225	225
Example 13	70	30	magnesium phenyl-phosphonate	0.1	77.9	-1.0	3.8	0.69	104	230	230
Example 14	70	30	potassium phosphinate	0.05	78.2	-0.2	4.2	0.70	105	225	225
Example 15	60	40	sodium dimethyl phosphinate	0.1	75.2	-1.1	3.7	0.68	112	220	220
Example 16	60	40	tribenzyl phosphite	0.05	74.3	-0.2	3.5	0.68	111	222	222
Example 17	70	30	tri(hydroxy-ethyl) phosphate	0.1	74.1	-0.2	3.4	0.70	104	215	215
Comparative Example 1	70	30	—	—	70.3	0.4	13.3	0.70	104	220	220
Comparative Example 2	70	30	disodium phosphate	3.5	72.3	-0.5	3.8	0.69	104	8	8
Comparative Example 3	70	30	2,6-di-t-butyl phenol	1.0	69.5	0.5	16.3	0.70	105	225	225

It is seen from the above table that the composition not containing the phosphorus compound has a high b value and is strongly yellowish, whereas the composition of this invention containing the phosphorus compound has a markedly reduced b value in spite of having substantially the same intrinsic viscosity as the composition not containing the phosphorus compound, and exhibits an improved color. Furthermore, it can be seen from the table that the composition not containing the phosphorus compound assumes strongly yellowish color in spite of showing no substantial reduction in intrinsic viscosity. Accordingly, this demonstrates that the coloration of the composition does not occur as a result of the heat degradation of the composition, but is caused by mixing the polycarbonate with the poly(tetramethylene terephthalate).

Table 1 further shows that when the phosphorus compound is added in a larger amount than that specified in the present invention, the elongation of the composition is extremely reduced, and that a stabilizer such as 2,6-di-t-butyl phenol does not produce the effect of the present invention.

Example 18.

0.2 part of triphenyl phosphite was added to 100 parts of the composition of Comparative Example 1, and the mixture was melt-mixed and extruded at 250°C. using an extruder to form pellets (cylindrical pellets each having a diameter of about 1.5 mm, and a length of about 5 mm). The color of the pellets was remarkably improved over the pellets obtained in Comparative Example 1, with an L value of 70.5, an a value of 0.9, and a b value of 5.1.

Example 19 and Comparative Example 4.

80 Parts of poly(tetramethylene-2,6-naphthalene dicarboxylate) (having an intrinsic viscosity of 0.75 and containing about 0.03 mol%, based on polymer, of titanium tetrabutoxide), 20 parts of a polycarbonate of 2,2-bis(4-hydroxyphenylpropane) (intrinsic viscosity 0.68), and 0.1 part of monosodium phosphate were well mixed, and extruded at 270°C. using an extruder to form pellets (cylindrical pellets each having a diameter of about 1.5 mm and a length of about 5 mm).

The pellets obtained had an L value of 78.2, an a value of 1.0, and a b value of 2.7, and also an intrinsic viscosity of 0.73.

For comparison, the above procedure was repeated except that the monosodium phosphate was not used. The pellets had an intrinsic viscosity of 0.73, and an L value of 69.8, an a value of 0.5, and a b value of 12.5. This indicated that the color of the pellets was far inferior to that of the pellets obtained in accordance with the present invention.

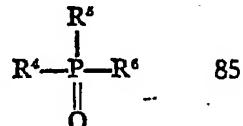
WHAT WE CLAIM IS:—

1. An aromatic polyester resin composition with inhibited coloration, which comprises:

(1) 100 parts by weight of an aromatic polyester resin derived from a glycol component at least 70 mol % of which consists of tetramethylene glycol and an acid component at least 70 mol % of which consists of isophthalic acid, terephthalic acid, a naphthalene dicarboxylic acid, or a polyester-forming derivative thereof, which components are polymerized with a titanium compound catalyst.

(2) 5 to 100 parts by weight of a polycarbonate resin per 100 parts by weight of the aromatic polyester resin, and

(3) 0.01 to 3 parts by weight per 100 parts by weight of the aromatic polyester resin of at least one phosphorus compound which is liquid or solid at room temperature and is of formula:



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wherein each of R¹ to R⁶ independently represents hydrogen, alkyl of up to 20 carbon atoms, aryl of 6 to 20 carbon atoms, aralkyl of 7 to 20 carbon atoms, or —OR in which R is hydrogen, alkyl, hydroxyalkyl or cycloalkyl of up to 20 carbon atoms, aryl of 6 to 20 carbon atoms, or aralkyl of 7 to 20 carbon atoms; or at least two of R¹, R² and R³, or R⁴, R⁵ and R⁶ together with the phosphorus atom to which they are attached form a ring, and/or a metal salt thereof.

2. A composition according to claim 1 wherein the intrinsic viscosity of the aromatic resin is 0.3 to 1.5.

3. A composition according to claim 1 or 2 wherein the amount of the phosphorus compound is 0.02 to 0.5 part by weight per 100 parts by weight of the aromatic polyester resin.

4. A composition according to any preceding claim wherein the phosphorus compound is phosphoric acid, trimethyl phosphate, methyl-diethyl phosphate, triethyl phosphate, triisopropyl phosphate, tributyl phosphate, tri-phenyl phosphate, tribenzyl phosphate, tri-cyclohexyl phosphate, phosphorous acid, trimethyl phosphite, triethyl phosphite, tributyl phosphite, tri(δ-hydroxybutyl) phosphate, tri-phenyl phosphite, phosphonic acid, phenyl-phosphonic acid, phenyl phenylphosphonate, diphenyl phenylphosphonate, phosphinic acid, phenylphosphinic acid, methyl dimethylphosphinate, phenyl methylphosphinate, tri-phenyl phosphine, triphenyl phosphine oxide,

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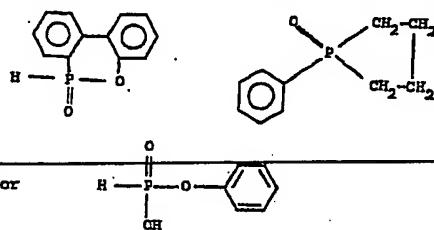
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5. A composition according to any of claims 1 to 3, wherein the phosphorus compound is a metal salt formed between phosphoric acid, phosphorous acid, phosphonic acid, phosphonous acid, phosphinic acid, phosphinous acid, substituted phosphonic acid, di- or mono-substituted phosphinous acid and lithium, sodium, potassium, rubidium, caesium, magnesium, calcium, strontium, barium, manganese, iron, cobalt, nickel, zinc, silver, cadmium, aluminium, tin, or lead.

10. 6. A composition according to claim 1, substantially as described in any one of the Examples.

15. 7. A method for inhibiting the coloration of an aromatic polyester resin composition comprising (1) 100 parts by weight of an aro-

matic polyester resin derived from a glycol component at least 70 mol % of which consists of tetramethylene glycol and an acid component at least 70 mol % of which consists of isophthalic acid, terephthalic acid, a naphthalene dicarboxylic acid, or a polyester forming derivative thereof which are polymerized with a titanium compound catalyst, and (2) 5 to 100 parts by weight of a polycarbonate resin, which method comprises incorporating into said composition 0.01 to 3 parts by weight per 100 parts by weight of the aromatic resin of at least one phosphorus compound of formula I or II, as defined in claim 1, before completion of melt-shaping of said composition.

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8. A method according to claim 7 substantially as described in any one of the Examples.

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9. An aromatic polyester resin composition with inhibited colouration, when obtained by a method as claimed in claim 7 or 8.

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